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14. ABSTRACT
High performance polyimides are currently utilized in a number of aerospace and microelectronic applications. Due to the inherent electronic polarity of the monomers used to synthesize many of these materials, resultant polymers often suffer from property degradation due to exposure to humid conditions, especially at elevated temperatures, often compromising their capabilities in service. The use of monomers demonstrating reduced susceptibility to hydrogen bonding with water molecules without sacrificing mechanical properties and thermo-oxidative stability would afford a new class of polyimide materials for applications currently inaccessible by the state-of-the-art. Thermoplastic polyimides reactively modified with polyhedral oligomeric silsesquioxanes have been found to exhibit a lower propensity for moisture absorption and concomitant property knockdown than their commercial analogues. Using this technology as a foundation, the objective of this work is to examine the effects of incorporating silsesquioxane anilines into the backbones of thermosetting polyimides, particularly elucidating influences on melt processing, curing kinetics, and delivered properties in the cured state. In particular, polymers synthesized from 4,4'-(hexafluoroisopropylidene)-diphthalic anhydride (6FDA) and 4,4'-oxydianiline have been shown to exhibit relatively high moisture uptake in comparison with many other polyimides. As such, these monomers have been selected to construct the backbone of the oligomers used in this study.

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PROPERTIES OF POSS-MODIFIED OLIGOIMIDE RESINS

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ABSTRACT

High performance polyimides are currently utilized in a number of aerospace and microelectronic applications. Due to the inherent electronic polarity of the monomers used to synthesize many of these materials, resultant polymers often suffer from property degradation due to exposure to humid conditions, especially at elevated temperatures, often compromising their capabilities in service. The use of monomers demonstrating reduced susceptibility to hydrogen bonding with water molecules without sacrificing mechanical properties and thermo-oxidative stability would afford a new class of polyimide materials for applications currently inaccessible by the state-of-the-art. Thermoplastic polyimides reactively modified with polyhedral oligomeric silsesquioxanes have been found to exhibit a lower propensity for moisture absorption and concomitant property knockdown than their commercial analogues. Using this technology as a foundation, the objective of this work is to examine the effects of incorporating silsesquioxane anilines into the backbones of thermosetting polyimides, particularly elucidating influences on melt processing, curing kinetics, and delivered properties in the cured state. In particular, polymers synthesized from 4,4'-(hexafluoroisopropylidene)-diphthalic anhydride (6FDA) and 4,4'-oxydianiline have been shown to exhibit relatively high moisture uptake in comparison with many other polyimides. As such, these monomers have been selected to construct the backbone of the oligomers used in this study.

1. INTRODUCTION

High performance polyimides are utilized in a number of aerospace and microelectronic applications requiring thin films, wire coatings, adhesives, and matrices for fiber reinforced composites.[1-3] In general, thermoplastic polyimides are produced from reactions between aromatic diamines and dianhydrides to form polyamic acids which in turn are thermally imidized to yield desired polymers.[1] Due to inter-chain interactions and polymer chain rigidity, such materials are often intractable exhibiting viscosities prohibitive to the fabrication of components via melt processing. Limiting molecular weight through reactive endcapping promotes processability by improving solubility in solvents and reducing melt viscosity.[3] This approach also facilitates the precise design of thermosetting oligomers to deliver target properties once they are cured to form polymer networks.

Due to the inherent electronic polarity of the monomers used to synthesize most polyimides, resultant polymers suffer from property degradation due to exposure to humid conditions, especially at elevated temperatures, often compromising their capabilities in environments possessing those conditions. The use of monomers with less susceptibility to hydrogen bonding with water molecules without sacrificing crucial mechanical properties and thermo-oxidative stability would afford new polyimide materials for applications currently inaccessible by the state-of-the-art. Recent work by Kakimoto et. al. demonstrated that copolymerization of polyhedral oligomeric silsesquioxane (POSS) diamines into thermoplastic pyromellitic dianhydride-oxydiphenylene aniline (Kapton™) reduced its moisture uptake by 83% concurrently improving mechanical properties.[4] The objective of this work is to examine the effects of incorporating similar silsesquioxane anilines into the backbones of thermosetting polyimides, particularly elucidating influences on melt processing, curing kinetics, and delivered properties in the cured state. In particular, polymers synthesized from 4,4'-(hexafluoroisopropylidene)-diphthalic anhydride (6-FDA) and 4,4'-oxydianiline have been shown to exhibit relatively high moisture uptake in comparison with other polyimides,[5-6] therefore, these monomers have been selected to construct the backbone of the oligomers used in this study. The amic acid route to the formation of phenylethynyl-terminated imide oligomers similarly used by Chen et. al.[7] has been adopted in this work due to the insolubility of the chosen POSS monomers in alcohol.

2. EXPERIMENTATION

2.1 Materials

4, 4' – diaminodiphenylether (ODA) and 4,4'-(hexafluoroisopropylidiene) diphthalic anhydride (6-FDA) were purchased from Lancaster Synthesis Inc. Phenyl-ethynyl phthalic anhydride (PEPA) was generously donated by the Maverick Corporation. The ODA, 6-FDA and PEPA were all purified by sublimation. Cis- and trans-bis(aniline, methyl)siloxy-octaphenylsilsesquioxane were synthesized using a method previously reported by our research group.[8] 1-methyl-2-pyrrolidinone (NMP) and methanol were purchased from Sigma Aldrich and were used as received. HPLC grade chloroform was purchased from Burdick and Jackson and used as received.

2.2 Synthesis of Bis(aniline, methyl)siloxy-octaphenylsilsesquioxane and 6-FDA-ODA-POSS-PEPA Oligomers

Under a nitrogen atmosphere, in a 50 mL round-bottomed flask, phenylPOSS-tetrol, $Phenyl_8Si_8O_{10}(OH_4)$, (2.00g, 1.87 mmol) was suspended in 10 mL of anhydrous THF. To this stirred suspension, a solution of 4-[Bis(N, N-trimethylsilyl)phenylamino]methyldichlorosilane (1.376 g, 3.93 mmol) and NEt_3 (0.776 g, 7.67 mmol) in THF (10 mL) was slowly added in a drop-wise manner. After 30 minutes, the solution was filtered to remove NEt_3HCl (974 mg, 7.08 mmol, 95 % theoretical) and the solvent was removed under vacuum. Approximately 1 mL of diethylether was added to the product followed by 20 mL of MeOH to make a well-stirred suspension of white-colored intermediate. The trimethylsilyl groups were hydrolysed by the addition of 1 drop of concentrated acetic acid and 1 hour of stirring. The product was isolated by filtration and dried under a nitrogen stream to give a white powder in 77 % yield (1.922 g, 1.44 mmol), consisting of a mixture of cis and trans POSS isomers. ^{1}H NMR ($CDCl_3$, δ) 7.83-7.10 ppm (m, 44H), 6.60. ppm (m, 4H), 3.3 ppm (broad s, 4H, NH_2), 0.11 ppm (s, 6H). ^{29}Si NMR

(CDCl$_3$) -29.7, -78.2, -79.1, -79.3, -79.4 ppm. The reaction scheme for this POSS monomer is depicted in Figure 1.
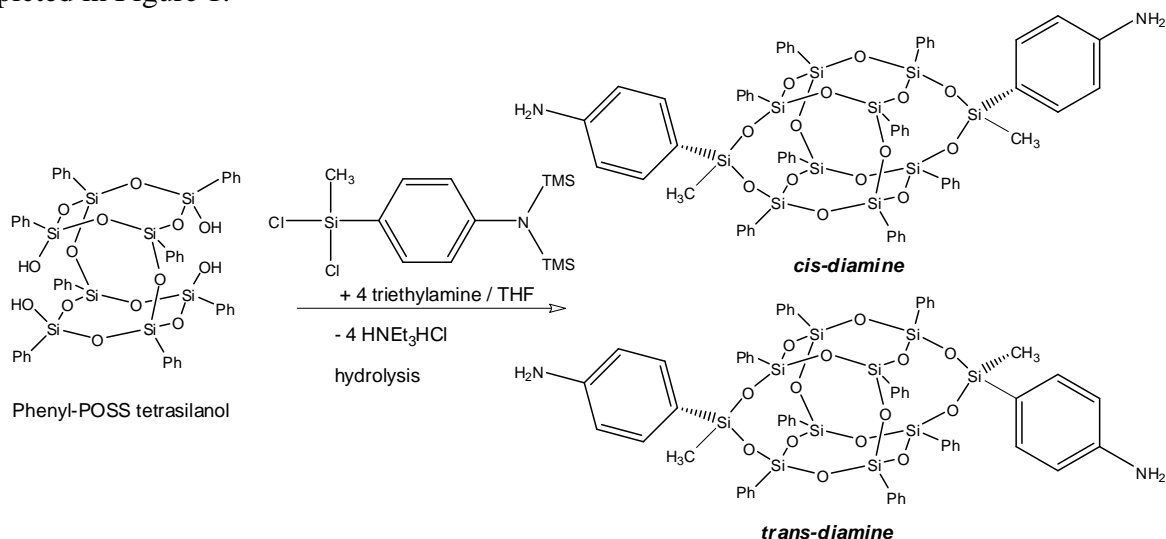

Figure 1. Reaction schematic for Bis(aniline, methyl)siloxy-octaphenylsilsesquioxane resulting in a mixture of cis and trans isomers.

2.3 Synthesis of 6-FDA-ODA-POSS-PEPA Oligoimides

According to the molar equivalents and weights of monomers shown in Tables 1 and 2, respectively, 6-FDA monomer was added to an NMP solution of ODA and/or POSS in a dry nitrogen environment. After allowing the reaction to proceed for 60 minutes, an NMP solution of PEPA was then added to produce a total concentration of 10 wt% solids. The reaction was allowed to stir overnight in a dry nitrogen environment. 15 mL of toluene was added and the reaction was heated to 155°C using the Dean-Stark methodology to promote imidization. FTIR data was taken at this point to ensure full imidization.[8] A solvent extraction to separate NMP from oligomer was then performed using 15 mL of chloroform and distilled water. Excess chloroform was removed under reduced pressure; the reaction mixture was then added drop-wise to methanol and allowed to stir overnight. The solid product was collected by filtration and washed with methanol.   The solid product was dried under vacuum and subsequently characterized by ^{1}H, ^{13}C, and ^{29}Si NMR.

Table 1. Equivalents of monomers used to synthesize each of the oligoimides.

Compound Mol. Wt. Formula	PEPA 248.23 C$_{16}$H$_8$O$_3$	6-FDA 444.24 C$_{19}$H$_6$F$_6$O$_6$	ODA 200.24 C12H12N2O	POSS 1335.98 C$_{62}$H$_{58}$N$_2$O$_{14}$Si$_{10}$
0 POSS	2	4	5	0
1 POSS	2	4	4	1
2 POSS	2	4	3	2
3 POSS	2	4	2	3
4 POSS	2	4	1	4
5 POSS	2	4	0	5

Table 2. Amounts of monomers used in each of the six oligoimides.

| Target Oligomer (Avg. mol. for.)	Molecular Weight	Mmoles in 7.00 g	PE (g)	6-FDA (g)	ODA (g)	POSS (g)	Wt. % $Si_{10}O_{14}$
$C_{168}H_{80}F_{24}N_{10}O_{25}$	3094.45	2.2624	1.1228	4.0194	2.2645	0.000	0.0%
$C_{218}H_{126}F_{24}N_{10}O_{38}Si_{10}$	4230.19	1.6548	0.8218	2.9407	1.3251	2.2106	8.33%
$C_{268}H_{172}F_{24}N_{10}O_{51}Si_{20}$	5365.94	1.3048	0.6475	2.3184	0.784	3.4853	13.16%
$C_{318}H_{218}F_{24}N_{10}O_{64}Si_{30}$	6501.69	1.0766	0.5348	1.9131	0.262	4.3148	16.31%
$C_{368}H_{264}F_{24}N_{10}O_{77}Si_{40}$	7637.44	0.9163	0.4550	2.3289	0.1834	4.8979	18.48%
$C_{418}H_{310}F_{24}N_{10}O_{90}Si_{50}$	8773.18	0.798	0.3962	1.4175	0.000	5.3298	20.16%
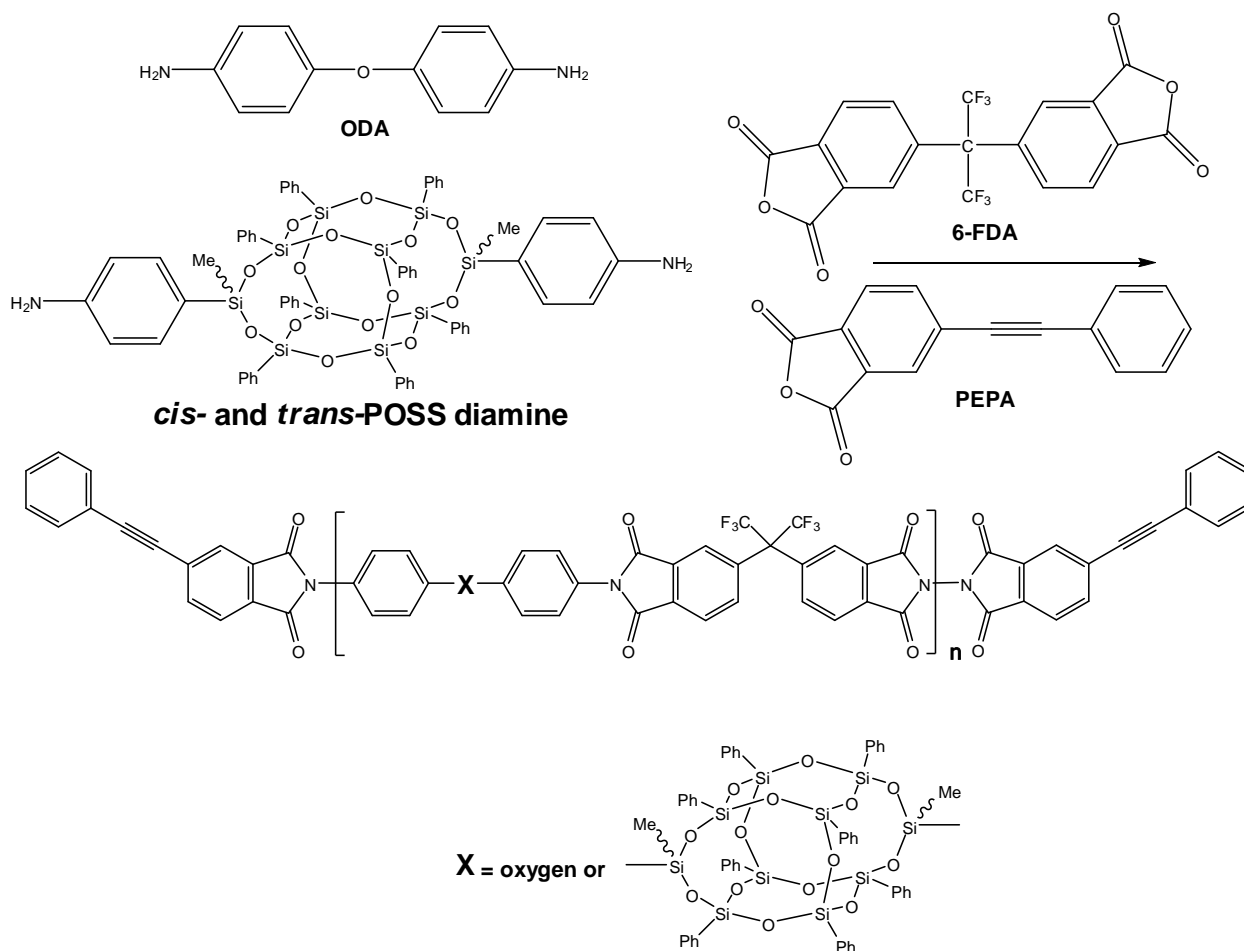
Figure 2. Chemical structures of monomers and resultant oligoimides.

2.4 Characterization Techniques

^1H, ^{13}C, and ^{29}Si nuclear magnetic resonance spectra were obtained on a Bruker 300 MHz spectrometer using 5 mm o.d. tubes. CDCl$_3$ and Me$_4$Si were used as internal and external reference standards, respectively.

3.   RESULTS

3.1 NMR Characterization of POSS Dianiline

The synthesis of the POSS dianiline beginning with a silsesquioxane tetrol resulted in a mixture of cis- and trans-isomers about the two D silicons which can be separated via crystallization. The ^{29}Si NMR spectra for the dichlorosilane, de-protected amine isomers, end product isomer mixture, and separated isomers are shown in Figure 3 (a-e). Hydrolysis of the trimethylsilyl groups causes a slight downfield shift of the signal corresponding to the peaks assigned to the two D silicon atoms. In the final products, three peaks assigned to the T silicon atoms of the silsesquioxane cage are prevalent for the cis-isomer, while only two signals are detected for the trans-isomer.
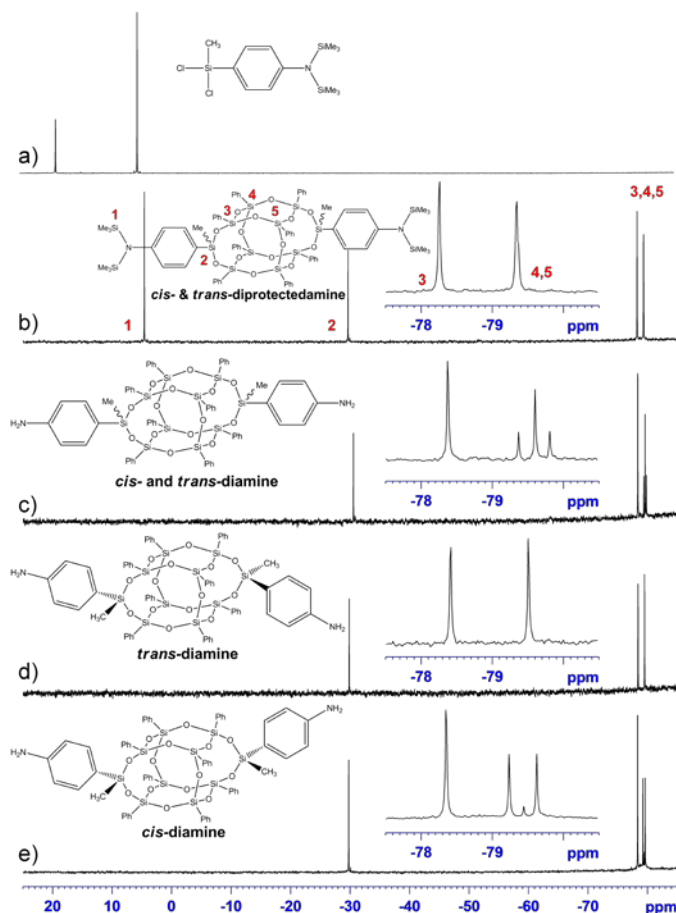

Figure 3. ^{29}Si NMR spectra of (a) 4-[bis(N, N-trimethylsilyl)phenylamino]-methyldichlorosilane, (b) cis- and trans-deprotected amines, (c) mixture of cis- and trans-diamine end product, (d) trans-diamine, and (e) cis-diamine.

3.2 NMR Characterization of Oligoimides

The silicon NMR of the oligoimides demonstrated sharp peaks at approximately 79 ppm, indicating that the POSS cages had not degraded during synthesis. In the ^{1}H NMR spectrum, the peaks between 0.00 ppm and 1.5 ppm are attributed to the two methyl groups on the POSS. The total ^{1}H integral was normalized to the expected number of protons for a particular oligomer (126 – 1 POSS; 172 – 2 POSS; 218 – 3 POSS; 264 – 4 POSS; 310 – 5 POSS). Relatively speaking, the integrals in the methyl region are shown to increase by 6 with each additional POSS. The peaks between 6.8 ppm and 7.8 ppm are attributed to the ODA, POSS and the 5 protons on one of the phenyl rings in PEPA. The integrals are shown to increase by the expected amount with each addition and reduction of POSS and ODA respectively. The final peaks from 7.8 ppm – 8.5 ppm are attributed to 6-FDA and 3 protons on one of the phenyl rings in PEPA. The integrals in this region stayed constant at 30 as the amount of end cap and 6-FDA did not vary.
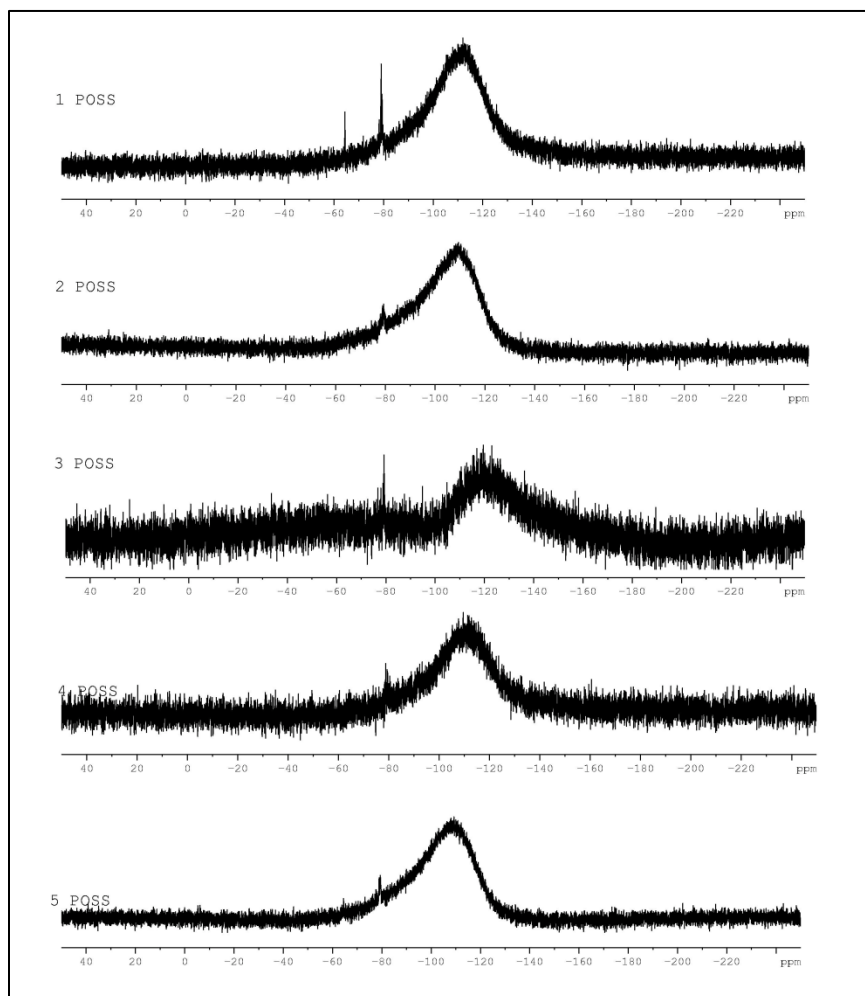

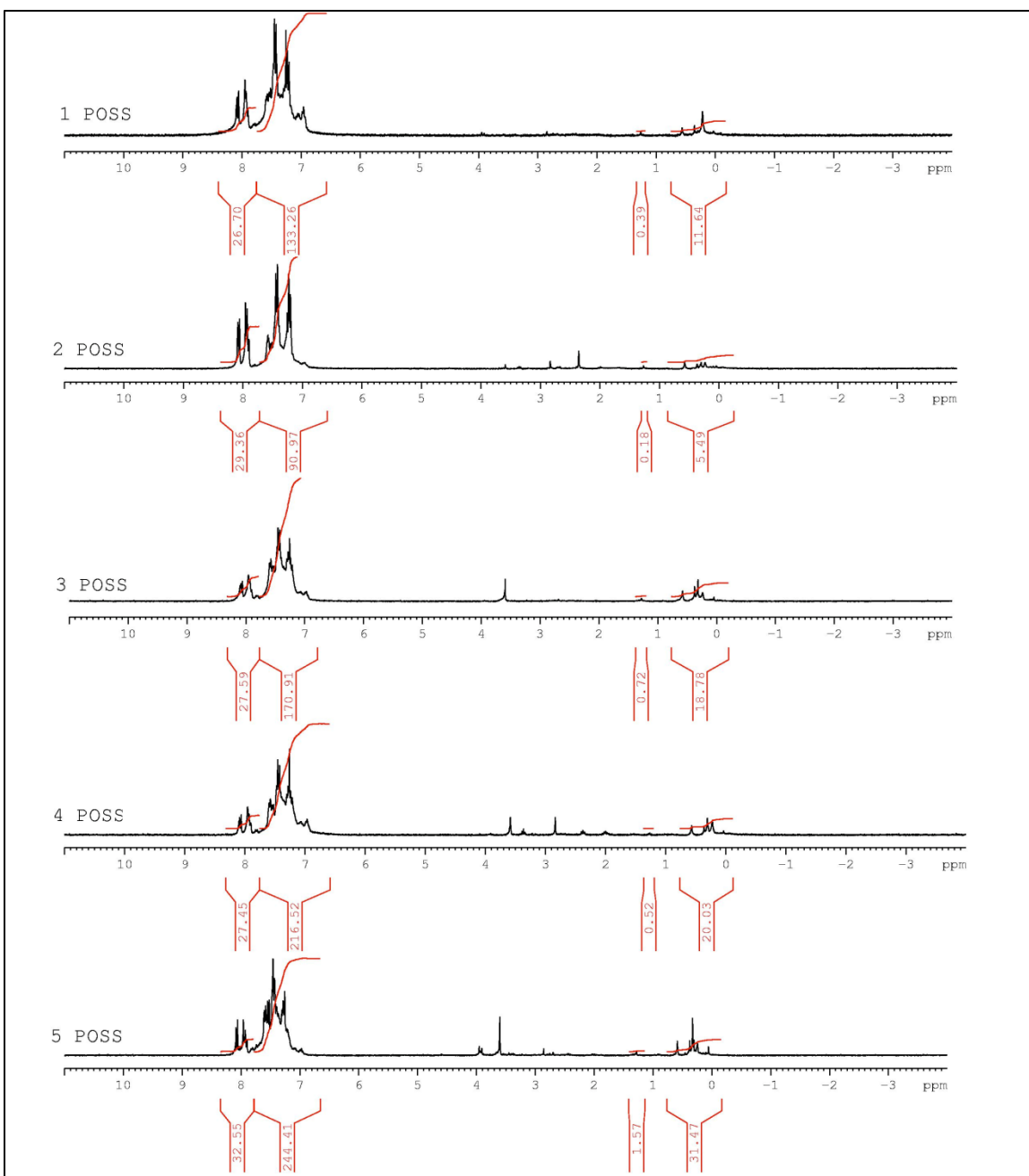Figure 4. ^{29}Si NMR of 1, 2, 3, 4 and 5 POSS containing oligoimides.

Figure 5. ^{1}H NMR of 1, 2, 3, 4 and 5 POSS oligoimides.

4. CONCLUSIONS

Thermosetting imide oligomers have been synthesized in high yield via a polyamic acid route. The oligomers contain 6-FDA and various ratios of the dianilines 4,4'-ODA and bis(aniline, methyl)siloxy-octaphenylsilsesquioxane end-capped with PEPA. NMR characterization of the oligoimides show that the POSS cages remain intact during oligomer synthesis and that targeted POSS contents in the five modified oligomers were achieved. Since the occupied volume of the POSS dianiline used in this study is so much larger than that of ODA and 6-FDA, it is expected

that its systematic incorporation will affect oligomer packing and the architectures of resultant crosslinked polymer networks thus impacting processability, cure kinetics, and end-use properties including those thermal, mechanical, and electrical in nature. Since the POSS monomer is intrinsically hydrophobic, its incorporation is also expected to influence moisture affinity. Full characterization of the oligomers and cured polymers is underway and will be reported at the conference.

5. ACKNOWLEDGEMENTS

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